Initial and Stressed Performance of CdTe Solar Cells: Effect of Contact Processing

S. S. Hegedus, B. E. McCandless and R.W. Birkmire
Institute of Energy Conversion
University of Delaware, Newark, DE 19716 USA

ABSTRACT

The relationship between back contact processing and electrical behavior of CdTe/CdS thin-film solar cells in initial and stress-degraded states is addressed. The back contact consists of a primary contact of Cu and Te components and a secondary contact for lateral current collection. The primary contact was formed by a sequential vapor process to: 1) remove residual oxides from $CdCl_2$ treatment; 2) deposit a Te layer; 3) deposit a Cu layer; and 4) react Cu and Te. Secondary contact was made with C ink or evaporated Ni or Mo. Variations in primary contact Cu-Te composition and total thickness and in choice of secondary contact were combined with electrical measurements to determine the effect on devices in initial and degraded states. Devices were stressed under controlled temperature, light bias, electrical bias, and ambient in the IEC stress system. Three degradation modes are identified with respect to the CdTe/CdS junction, formation of a blocking contact, and increasing photoconductivity in CdS and CdTe.

1. Background

CdTe/CdS modules in field testing scenarios are reported to be stable. However, no clear correlation has been found between processing parameters and either these stable existence-proof cases or those that changed in field testing. Recent work to accelerate these processes at the laboratory scale (stress testing) have shown that typically the V_{oc} and FF degrades, particularly for devices held at moderate forward or reverse bias. We have shown that there are at least three degradation mechanisms [1]. One is related to the junction and increases recombination which reduces V_{oc}, another is related to the CdTe contact and forms a blocking contact which reduces FF, and the third is an increase in the dark resistance which may have little effect on the illuminated solar cell. The back contact process is clearly related to all of the stress-induced degradation, especially with respect to the presence of Cu and its compounds, which are sensitive to small, localized fields in both electrochemical and electromigration processes. Both the *primary* contact, which often contains Cu-Te compounds and makes intimate contact with CdTe, and the *secondary* contact, which is the current-carrying robust contact layer, have been implicated in accelerated degradation studies (see Fig. 1). The contact process developed by IEC allows for separation of the process variables. IEC has constructed a system for the accelerated stressing of CdTe/CdS solar cells under carefully controlled conditions by exposure to thermal, chemical, electrical, and illumination bias. Stress conditions were typically 10 days in dry air, either at 60°C in the dark at -1V, 0V and +1V or 100°C in the light at -1V, SC, MP, and OC.

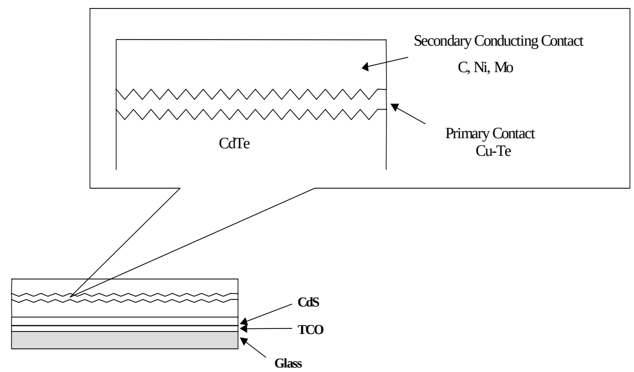

Fig. 1 Schematic of CdS/CdTe solar cell showing the primary and secondary contacts.

2. Effect of Bias and Atmosphere in Accelerated Stress

Based on a large number of samples and stress experiments, we find that devices biased during stress at short circuit (SC) lose ~50mV in V_{oc} and ~5% in FF, while those stressed at open circuit (OC) lose > 100 mV in V_{oc} and > 5% in FF (see Fig. 2). Some devices stressed at SC develop a large cross-over between the light and dark curves, indicating a large photoconductivity effect. Cu is strongly correlated to degradation at OC but not SC. Some but not all devices develop curvature in forward bias beyond OC, indicating that the CdTe contact has evolved from ohmic to blocking. Similar results for bias dependence and blocking contact formation have been found for cells with Cu that are stressed in H_2/Ar or Ar atmospheres or made with different CdTe surface processing. Devices without Cu have lower initial efficiency but are more stable and have very little stress bias dependence. Their V_{oc} may decrease only 20-40 mV with stress. Devices with Cu in the back contact can degrade in a few hours or days under forward bias of 1-2V at 60°C. This rapid change suggests that positive Cu ions move by field-driven diffusion along grain boundaries.

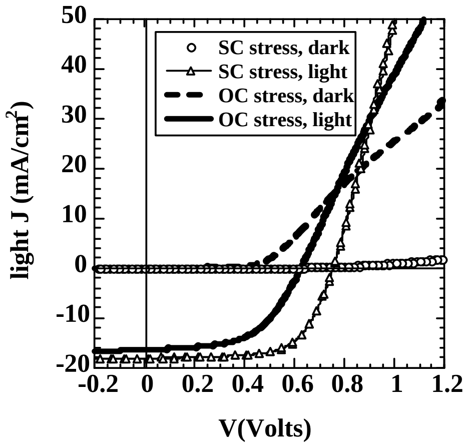

Fig. 2. Light and dark JV curves after SC and OC stress for 10 days at 100°C. Dark curve for SC stress is nearly horizontal.

3. Separating Junction and Contact Degradation

A CdS/CdTe solar cell having an initial efficiency of 11.8% and V_{oc} of 0.82V was stressed at OC at 100°C for 6 weeks in air at 2 suns, which reduced the efficiency to 7.2% and V_{oc} to 0.73V. J_o increased by 30X, from 3E-8 to 8E-7 mA/cm^2, but there was no change in A-factor of ~1.6. Curvature developed after stress in the JV curves (both light and dark) at forward bias, most likely due to a blocking contact. After stressing, the original carbon contact was peeled away, the CdTe surface was re-etched in weak bromine-methanol and a new C contact was applied. The efficiency increased to 9.1% with no change in V_{oc}, J_o and A. However, the blocking contact disappeared and the FF increased significantly. This clearly demonstrates that the blocking contact is associated with the back contact.

4. Separating Primary and Secondary Contacts

Recently, we studied the effect of 3 variables, the Cu and Te thickness (i.e., primary contact) and the secondary contact material. The Cu/Te ratio and thickness were varied to separate the effects of stoichiometry and thickness on device performance and stability. This group of samples investigates primary contacts which are Cu-free, Cu-deficient and Cu-excessive $Cu_{2-x}Te$, and Cu_2Te, as well as secondary contacts of Ni, Mo or C-paste which have different work functions. The CdTe surface was reacted in H_2 + Te vapor to reduce surface oxides. After depositing 10 or 100 nm Te layers and 2-90 nm Cu layers, the Cu-Te primary contact was formed by heating to react the Cu and Te. The secondary contact was then applied.

Results from devices with different back contacts provide several critical observations regarding the influence of primary and secondary contacts. *For primary contacts*: thicker layers of the Cu-Te compounds give higher initial and post-stress performance than thinner layers for a fixed Cu/Te ratio; higher initial performance and stability are correlated with Te thickness regardless of the Cu thickness; devices with thick Cu (90 nm) are relatively stable providing they have thick Te layers (110 nm) to react with; devices without a Cu layer are relatively stable but exhibit lower initial performance; Cu is essential to achieve V_{oc} > 0.75V and FF > 65%; and Te and Cu thickness and their post-contact anneal must be optimized for each secondary contact. *For secondary contacts*: devices with C contacts yield higher V_{oc} and J_{sc} compared to Mo and Ni contacts; and devices with Ni and Mo contacts degrade very rapidly in forward bias, in the presence of the Cu layer. Finally, any secondary contact is relatively stable without a Cu layer.

5. Phenomenological Model, Conclusions, and Future Work

We have found that there are at least 3 mechanisms which govern the behavior in CdTe/CdS devices under thermal and bias stress. One, which occurs at forward bias or OC, is Cu-related, field-driven, occurs in ~hours, greatly increases the recombination, and is partially reversible. The second, which is also Cu related, is the formation of a blocking contact. Another, which occurs under reverse bias, is much slower, may not be Cu related, and changes the photoconductivity of either the CdS or CdTe. We propose that Cu^{++} is liberated from the Cu_2Te layer and moves along grain boundaries under forward bias. The concentration-gradient driven diffusion lengths for Cu in bulk CdTe and along grain boundaries have been calculated for 1 hour at 100°C. Cu would move 0.3 µm in the bulk and 30 µm along grain boundaries. Clearly grain boundaries are important channels for Cu motion. But even devices without a Cu layer show some degradation indicating there are either low levels of Cu contamination in the CdTe or CdS, or that there is a non-Cu related degradation mechanism. The secondary contact can influence degradation by varying the amount of free Cu, since each contact has a different Cu solubility, and by varying the local electric field.

Future work will involve changing the way in which Cu is introduced to the processing, investigating much thicker Te layers, and attempting to link laboratory stressing with field data by simulating day-night cycling.

ACKNOWLEDGMENTS

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REFERENCES

[1] S. Hegedus, B. McCandless, and R. Birkmire, 28th IEEE PVSC (2000), pp. 535-538.